## 1

## APPARATUS AND METHOD FOR DIFFERENTIAL ANALYSIS USING REAL AND IMAGINARY SIGNAL COMPONENTS

### BACKGROUND OF THE INVENTION

The present invention relates to a method and apparatus for differential thermal analysis. Differential thermal techniques generally consist of applying heat simultaneously to a sample material and a reference material and measuring a parameter, such as differential power input, as the sample goes through a physical or chemical change. In differential thermal analysis (DTA), the sample and reference are heated or cooled according to a programmed rate, and the temperature differential between the sample and reference is measured as the scan proceeds. In differential scanning calorimetry (DSC), differential power rather than differential temperature is measured. The differential power represents the difference in energy required to maintain the sample and reference in accord with a heating or cooling program.

In addition to DSC and DTA, other differential thermal techniques also exist to measure basic properties that change with temperature. In differential dielectric analysis (DDA) a property of the sample (dielectric constant) is measured while the temperature is changed. Further, in differential thermogravimetric analysis (DTGA), differential weight loss of a sample is monitored as the temperature is increased.

In 1968, Sullivan and Seidel reported a non-differential thermal technique which is now known as AC calorimetry. P. F. Sullivan, G. Seidel, "Steady-State, AC-Temperature Calorimetry, " Phys. Rev. 173(3), 679–685 (1968). This technique was later modified by Dixon et al. who, in 1982, reported a method called differential AC calorimetry. G. S. Dixon et al., "A Differential AC Calorimeter for Biophysical Studies," Anal. Biochem. 121(1), 55–61 (1982). Differential AC calorimetry, as described by Dixon et al., consists of heating or cooling the sample and reference at a linear rate with a sinusoidal oscillation superimposed on the linear heating or cooling program. Dixon et al. determined the heat capacity of the sample using the differential AC temperature response measured between the sample and reference.

U.S. Pat. No. 5,224,775, assigned to TA Instruments, Inc. (hereinafter "the '775 patent"), discloses the use of differential AC calorimetry in a method which deconvolutes the resulting differential signal as described by Dixon et al. The '775 patent discloses processing of the signal into "rapidly reversing" and "non-rapidly reversing" components. The thermodynamic significance of the "rapidly reversing" and "non-rapidly reversing" components is not apparent for time-dependent processes. For time-independent thermal events (equilibrium processes), only the "rapidly reversing" component may have thermodynamic significance. Since most thermal events of interest, such as the glass transition of a polymeric material, are time-dependent processes, there is an obvious need for a more comprehensive method of processing the differential signal.

The present invention provides a method and apparatus for processing the differential signal into real (inphase) and imaginary (quadrature) components which are related to the "energy storage" and "energy loss" portions of the thermal event being studied. The inphase and quadrature components provide physical and thermodynamic information for thermal events which are time-independent or time-dependent.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram illustrating a "power compensation" differential scanning calorimeter, which

## 2

includes two control loops and is adapted to implement the present invention.

FIG. 2 is a schematic diagram illustrating a DTA instrument which is adapted to implement the present invention.

FIG. 3 is a schematic diagram illustrating a "heat flux" differential scanning calorimeter which is adapted to implement the present invention.

FIG. 4 is a plot of heat capacity vs. temperature with data representing average heat capacity, the energy storage (real) portion of the heat capacity and the energy loss (imaginary) portion of the heat capacity which are obtained according to the method and apparatus of the present invention.

FIG. 5 is a plot of heat capacity vs. temperature with data representing average heat capacity, the absolute value of the heat capacity and the difference between the average and absolute heat capacity.

FIG. 6 is a plot of heat capacity vs. temperature with data representing the energy loss (imaginary) and energy storage (real) portions of the heat capacity, the absolute value of the heat capacity and the difference between the average and absolute heat capacity which are obtained according to the method and apparatus of the present invention.

FIG. 7 is a plot of heat capacity vs. temperature with data representing the energy loss (imaginary) and energy storage (real) portions of the heat capacity, and the average heat capacity which are obtained according to the method and apparatus of the present invention.

FIG. 8 is a plot of heat capacity vs. temperature with data representing the energy loss (imaginary) and energy storage (real) portions of the heat capacity, the absolute and average values of the heat capacity and the difference between the average and absolute heat capacity.

FIG. 9 is a plot of heat capacity vs. temperature with data representing the energy loss (imaginary) and energy storage (real) portions of the heat capacity, and the average heat capacity which are obtained according to the method and apparatus of the present invention.

FIG. 10 is a plot of heat capacity vs. temperature with data representing the absolute and average values of the heat capacity and the difference between the average and absolute heat capacity.

FIG. 11 is a plot of heat capacity vs. temperature with data representing the energy loss (imaginary) and energy storage (real) portions of the heat capacity, the absolute and average values of the heat capacity and the difference between the average and absolute heat capacity.

FIG. 12 is a graph representing an interpolation method for determining $\phi_g$.

### SUMMARY OF THE INVENTION

The invention is directed to a differential analysis apparatus comprising (i) a sample holder and a reference holder, (ii) a thermal device for subjecting the sample and reference to an externally applied disturbance, such as temperature change, in accord with a prescribed function comprising the sum of a linearly changing part and a periodically changing part (iii) at least one computing device for receiving data representative of differential signals resulting from the sample and reference being subjected to the applied disturbance in accord with the prescribed function, and (iv) a device to process said data to provide at least one parameter, such as heat capacity, representative of said sample and to separate said at least one parameter into components relating